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(54) **Polysaccharide aldehydes prepared by oxidation method and used as strength additives in papermaking**

Polysaccharid-Aldehyde hergestellt durch ein Oxidationsverfahren und verwendet als Festigkeitszusatzstoffe für die Papierherstellung

Polysaccharide-aldehydes préparés par un procédé d'oxydation et utilisés en résistance pour la fabrication de papier

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WO-A-00/50462	WO-A-00/50463
WO-A-99/23117	DE-C- 19 746 805
US-A- 3 203 885	US-A- 3 450 692
US-A- 3 691 153	US-A- 5 700 917

- PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 012301 A (MITSUBISHI GAS CHEM CO INC), 19 January 1999 (1999-01-19)
- ANELLI P L ET AL: "FAST AND SELECTIVE OXIDATION OF PRIMARY ALCOHOLS TO ALDEHYDES OR TO CARBOXYLIC ACIDS AND OF SECONDARY ALCOHOLS TO KETONES MEDIATED BY OXOAMMONIUM SALTS UNDER TWO-PHASE CONDITIONS" JOURNAL OF ORGANIC CHEMISTRY, US, AMERICAN CHEMICAL SOCIETY, EASTON, vol. 52, no. 12, 12 June 1987 (1987-06-12), pages 2559-2562, XP000567759 ISSN: 0022-3263

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## Description

## BACKGROUND OF THE INVENTION

- 5 [0001] This invention relates to the preparation of polysaccharide aldehydes using selective oxidation conditions. More particularly, this invention involves the preparation of polysaccharide aldehyde derivatives using nitroxyl radical mediated aqueous oxidation with a limited amount of oxidant and defined reaction conditions to provide derivatives with maximum effective aldehyde and minimal carboxylic acid content. This invention further involves the use of these selectively prepared polysaccharide aldehydes as strength additives in papermaking.
- 10 [0002] The term "paper" as used herein, includes sheet-like masses and molded products made from fibrous cellulosic material which may be derived from natural sources, synthetics such as polyamides, polyesters, rayon and polyacrylic resins as well as from mineral fibers such as asbestos and glass. In addition, paper made from combinations of cellulosic and synthetic materials are applicable herein. Paperboard is also included within the broad term "paper".
- 15 [0003] The preparation of aldehyde containing polysaccharides and the use of such aldehyde derivatives as wet and dry strength additives in the paper industry is well known. Oxidative and non-oxidative methods have been used to introduce aldehyde groups into polysaccharides such as starches, gums and celluloses. Oxidative methods are well known for introducing aldehyde groups into polysaccharides such as starch. These oxidative methods have included: a) treatment of starch with alkali metal bromite or hypobromite under carefully controlled conditions as disclosed in U.S. Patent No. 3,553,193 issued January 5, 1971 to D. H. Leroy et al.; b) oxidizing a carbohydrate with an alkali metal ferrate as shown in U.S. Patent No. 3,632,802 issued January 4, 1972 to J. N. BeMiller, c) enzymatically oxidizing hydroxypropyl galactoglycoside starch ethers or ethyl galactoglycoside starch ethers with galactose oxidase as disclosed in U.S. Patent No. 4,663,448 issued May 5, 1987 to C. W. Chiu; and d) treatment with periodic acid or periodates as disclosed in U.S. Patent No. 3,096,969 issued to J. E. Slager on April 23, 1963 which shows the preparation of dialdehyde polysaccharide using periodic acid and U.S. Patent No. 3,062,652 issued on November 6, 1962 to R. A. Jeffreys et al. which shows the preparation of dialdehyde gums using periodate or periodic acid.
- 25 [0004] Oxidative methods often cause degradation of the polysaccharide and the formation of excess carboxyl groups. Excess carboxyl groups undesirably reduces the degree of aldehyde substitution and negatively affects the cationic/anionic balance of the functional groups when using a cationic polysaccharide base in papermaking applications.
- 30 [0005] The use of nitroxyl radicals and nitrosonium salts in organic chemistry as an oxidative route to access aldehydes and carboxylic acids from primary and secondary alcohols is disclosed in an article entitled "Organic Nitrosonium Salts As Oxidants in Organic Chemistry" by J. M. Bobbitt and C. L. Flores, in Heterocycles, Vol. 27, No. 2, 1988, pp. 509-533. Recently, application of this chemistry was extended to the selective oxidation of primary alcohols in various carbohydrates to carboxylic acids in an article entitled "Selective Oxidation of Primary Alcohols Mediated by Nitroxyl Radical in Aqueous Solution. Kinetics and Mechanism" by A. E. J. de Nooy and A. C. Bessemer, in Tetrahedron, Vol. 51, No. 29, 1995, pp. 8023-8032. Patent publication WO 95/07303 dated March 16, 1995 further discloses the use of this technology where carbohydrates having a primary hydroxyl group are oxidized under aqueous conditions to form products having a high content of greater than 90% carboxyl groups. This art involving the oxidation of primary alcohols generally describes the preparation of polyglucuronic acids with high carboxylic acid content. Similarly, the process of oxidation has been used to prepare various polysaccharides with high carboxyl content as described in "Oxidation of Primary Alcohol Groups of Naturally Occurring Polysaccharides with 2,2,6,6-Tetramethyl-1-piperidine Oxoammonium ion" by P. S. Chang and J. F. Robyt in J. Carbohydrate Chemistry, 15(7), 1996, pp. 819-830. It should be noted that in some applications high carboxylic content is undesirable.
- 40 [0006] A recent patent publication, WO 99/23240 dated May 14, 1999 discloses a method for producing oxidized starch using an oxoammonium ion producing reagent in the presence of an enzyme oxidizing agent. Polysaccharide aldehydes may also be prepared by non-oxidative methods which typically involve the reaction of a polysaccharide with an aldehyde containing reagent. For example, U.S. Patent No. 4,675,394 issued to D. Solarek et al. on June 23, 1987 discloses a non-oxidative method wherein polysaccharide is reacted with a derivatizing acetal reagent in the presence of alkali to provide the stable acetal polysaccharide. The general disadvantage of these non-oxidative approaches is that they often require an extra conversion step to the aldehyde. For example, the polysaccharide acetals need to be cooked or pre-treated under acidic conditions to form the aldehyde just prior to its use.
- 50 [0007] US-A-3 450 692 discloses a process for the production of oxidized starch derivatives with a ratio of carbonyl to carboxyl radicals ranging from 0.3-2.5 carbonyl to 1.0 carboxyl.
- [0008] US-A-3 691 153 is directed to additives to promote the wet strength in paper making and non-cellulosic polysaccharide such as guar gums which have been oxidized to aldehyde groups without simultaneous ring opening of the modified hexose units.
- 55 [0009] US-A-5 700 917 discloses aldehyde cationic polysaccharide that are said to be useful as paper additives to improve dry and wet strength.
- [0010] In J. Org. Chem. 1987, vol. 52, no. 12, 1987 p. 2559-2562 a process for the fast and selective oxidation of

primary alcohols to aldehydes by mediation by oxo ammonium salts in a few minutes at 0°C under aqueous organic two-phase conditions is disclosed.

[0011] DE-A-197 46 805 discloses the preparation of oxidized starch by reaction with a hypohalite in the presence of a nitroxyl compound at a pH value smaller or equal than 8.5 and a temperature between 0 and 35°C.

5 [0012] WO-A-99/23117 is directed to a method for preparing oxidized cellulose. The method comprises bringing a cellulose containing material in contact with a reactant, such as 2,2,6,6-tetramethylpiperidine-1-oxyl, producing oxoammonium ion in the presence of an oxidizing agent and at room temperature. The oxidized pulps are said to be useful for preparing paper having improved strength properties.

10 [0013] What is desired is a direct and selective oxidation route to polysaccharide aldehyde derivatives wherein the aldehydes are formed at maximum effective levels and carboxylic acid levels are minimized making such aldehyde derivatives especially useful as wet, temporary wet and dry strength additives for paper.

## SUMMARY OF THE INVENTION

15 [0014] Now It has been found that polysaccharide aldehydes can be selectively prepared under defined oxidation conditions using a nitroxyl radical mediated aqueous oxidation procedure to provide derivatives with maximum effective aldehyde and minimal carboxylic acid content

[0015] More particularly, this invention involves the oxidation of a polysaccharide in an aqueous solution with an oxidant having an equivalent oxidizing power of up to 14.18 g active chlorine per mole of polysaccharideanhydrosugar unit ("ASU") and from 0.001 to 20 mole %, based on the moles of polysaccharide ASU of nitroxyl radical, the reaction  
20 being carried out by slow and controlled addition of the oxidant to the aqueous slurry or solution of the polysaccharide containing the nitroxyl radical so as to keep the temperature at or below about 15°C and the pH of from about 8.0 to 10.5 and the resulting product having up to about 15 mole % of C-6 aldehyde groups per mole of polysaccharide ASU and minimal carboxylic acid content. A polysaccharide ASU is defined to be the monosaccharide residues from which  
25 linear or branched polysaccharides can be seen to be constructed by a series of condensation reactions.

[0016] The polysaccharide aldehyde derivatives are useful in conventional applications where water-soluble or water-swellaable polysaccharide derivatives are useful, for example, as coatings, adhesives and paper additives. The cationic aldehyde containing derivatives are particularly useful as wet, temporary wet and dry strength additives for all paper  
30 types including liner board.

## DETAILED DESCRIPTION OF THE INVENTION

[0017] This invention involves the selective oxidation of polysaccharides in an aqueous system using a limited amount of oxidant with a nitroxyl radical mediator under defined conditions. The prepared products are highly selectively oxidized  
35 polysaccharides where there is a high level of C-6 aldehyde functionality with minimal carboxylic acid and are particularly suitable as wet, temporary wet and dry strength paper additives.

[0018] When the polysaccharide is starch, the starch base material useful in this Invention may be any of several starches, native or modified. Such starches include those derived from any plant source including, corn, potato, sweet potato, wheat, rice, tapioca, waxy maize, sago, sorghum and high amylose starch such as high amylose corn, i.e., starch  
40 having at least 45% by weight of amylose content. Starch flours may also be used as a starch source. Also included are the conversion products derived from any of the former bases including, for example, dextrans prepared by the hydrolytic action of acid and/or heat; fluidity or thin-boiling starches prepared by enzyme conversion or mild acid hydrolysis; and derivatized and crosslinked starches.

[0019] The starch may be modified with cationic, anionic, amphoteric, zwitterionic, hydrophobic and nonionic groups and combinations of such groups. It is preferred that the starch is modified with a cationic group. Cationization of the starch can be produced by well known chemical reactions with reagents containing groups such as amino, imino, ammonium, sulfonium or phosphonium groups as disclosed, for example in "Cationic Starches" by D. B. Solarek, in  
45 Modified Starches: Properties and Uses, Chapter 8, 1986 and in U.S. Patent No. 4,119,487 issued October 10, 1978 to M. Tessler. Such cationic derivatives include those containing nitrogen containing groups comprising primary, secondary, tertiary and quaternary amines and sulfonium and phosphonium groups attached through either ether or ester  
50 linkages. Particularly useful cationic starch derivatives are those containing amino or nitrogen groups having alkyl, aryl, alkaryl, aralkyl or cyclic substituents of 1 to 22 carbon atoms and especially 1 to 6 carbon atoms. Preferred derivatives are those containing tertiary amino and quaternary ammonium ether groups.

[0020] When the polysaccharide is a gum, the applicable bases which may be used herein include polygalactomannans, which are heteropolysaccharides composed principally of long chains of  $\beta$ -D-mannopyranosyl units to which single unit  
55 side chains of  $\alpha$ -D-galactopyranosyl units are joined. Also included are degraded gum products, resulting from the hydrolytic action of acid, heat, shear and/or enzyme, oxidized gums, and derivatized gums. The preferred gums include, guar, locust bean, tara and fenugreek gums. Other suitable polysaccharide bases that may be used in this invention

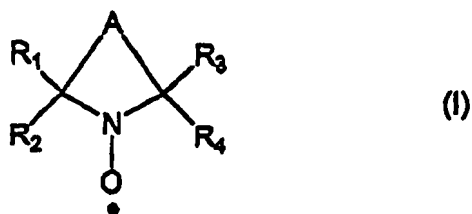
include, but not limited to, pullulan, chitin, chitdsan, gum arabic, agar, algin, carrageenan, xanthan, gellan, welan, rham-san, curdlan scleroglucan, tamarind gum, and hemicelluloses such as arabinogalactans and corn fiber gum and their derivatives.

**[0021]** When the polysaccharide is cellulose, applicable bases useful herein include cellulose and cellulose derivatives, especially water soluble cellulose ethers, such as carboxymethyl cellulose and alkyl and hydroxyalkylcelluloses, for example, methylcellulose, hydroxypropylmethylcellulose, hydroxyethylcellulose, hydroxyethylmethylcellulose, hydroxybutylmethylcellulose, and ethylhydroxyethylcellulose.

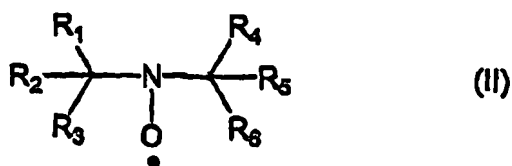
**[0022]** Methods for preparing the modified polysaccharide bases are well known to those skilled in the art and discussed in the literature. See, for example, R. L. Whistler, *Methods in Carbohydrate Chemistry*, Vol. IV, 1964, pp. 279-311; R. L. Whistler et al, *Starch Chemistry and Technology*, Vol. II, 1967, pp. 293-430, R. L. Whistler and J. N. Bemiller (Eds.), *Industrial Gums* 3<sup>rd</sup> Ed., 1993, Chapter 3, R. L. Davidson and N. Sittig, *Water Soluble Resins*, 2<sup>nd</sup> Ed., 1968, Chapter 2; and R. L. Davidson, *Handbook of Water Soluble Gums and Resins*. 1980.

**[0023]** The polysaccharide C-6 aldehydes prepared in accordance with this invention are obtained by a selective oxidation process. This oxidation reaction is carried out in an aqueous system using a limited amount of oxidant with a nitroxyl radical mediator under defined conditions. This defined reaction provides polysaccharide aldehydes where the aldehyde groups remain largely intact without being further oxidized to carboxylic acid residues.

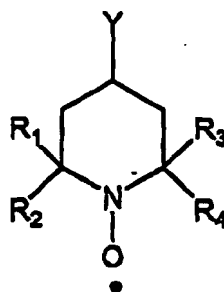
**[0024]** The nitroxyl radical mediator used herein is a di-tertiary alkyl nitroxyl radical having one of the following formulas:



or



where A represents a chain of preferably two or three atoms, in particular carbon atoms or a combination of one or two carbon atoms with an oxygen or nitrogen atom, and the R groups represent the same or different alkyl groups. Chain A may be substituted by one or more groups such as alkyl, alkoxy, aryl, aryloxy, amino, amido or oxo groups, or by a divalent group or multivalent group which is bound to one or more other groups having formula I. Particularly useful nitroxyl radicals are di-tertiary alkyl nitroxyl radicals having the formula:



where Y is H, OH or  $\text{NH-C(O)-CH}_3$  and each of the R groups represent the same or different alkyl groups of 1 to 18 carbon atoms and more particularly methyl groups. Nitroxyl radicals of this type include those where a) the R groups are all methyl (or alkyl of 1 carbon atom) and Y is H, i.e., 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO); b) R groups are methyl and Y is OH and identified as 4-hydroxy-TEMPO; and c) R groups are methyl and Y is  $\text{NH-C(O)-CH}_3$  and identified as 4-acetamido-TEMPO. The preferred nitroxyl radical is TEMPO or 4-acetamido-TEMPO. The nitroxyl radical is used in an effective amount to mediate the oxidation, particularly from about 0.001 to 20 mole %, and more particularly from about 0.01 to 5 mole % based on the moles of polysaccharide ASU. The nitroxyl radical can be added to the reaction mixture or generated in situ from the corresponding hydroxylamine or oxoammonium salts.

**[0025]** The oxidant used in this invention can be any material capable of converting nitroxyl radicals to their corresponding oxoammonium salt. Particularly useful oxidants are the alkali or alkaline-earth metal hypochlorite salts such as sodium hypochlorite, lithium hypochlorite, potassium hypochlorite or calcium hypochlorite. An alkali or alkaline-earth metal hypobromite salt may also be used, and it may be added in the form of the hypobromite salt itself, such as sodium hypobromite, or it may be formed in situ from the addition of a suitable oxidant such as sodium hypochlorite and an alkali or alkaline-earth metal bromide salt. Additional oxidants that can be used in this method include hydrogen peroxide in combination with a transition metal catalyst such as methyltrioxorhenium (VII); hydrogen peroxide in combination with an enzyme; oxygen in combination with a transition metal catalyst; oxygen in combination with an enzyme; peroxyacids such as peracetic acid and 3-chloroperoxybenzoic acid; alkali or alkaline-earth metal salts of persulfates such as potassium persulfate and sodium persulfate; alkali or alkaline-earth metal salts of peroxymonosulfates such as potassium peroxymonosulfate; chloramines such as 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)trione, 1,3-dichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)trione sodium salt, 1,3-dichloro-6,5-dimethylhydantoin, 1-bromo-chloro-5,5-dimethylhydantoin, and 1-chloro-2,5-pyrrolidinedione; and alkali or alkaline-earth metal salts of ferricyanide. This list of oxidants is only illustrative and is not intended to be exhaustive. The oxidants can be used alone or in combination with an alkali or alkaline-earth metal bromide salt. The preferred oxidant is sodium hypochlorite or sodium hypobromite formed from the addition of sodium hypochlorite and sodium bromide.

**[0026]** The important factor in the use of the oxidant is that it must be used in a limited amount that has the equivalent oxidizing power of up to 14.18 g active chlorine per mole of polysaccharide ASU. More particularly, the amount of oxidant used will have an equivalent oxidizing power of from about 0.35 to 14.18 g of active chlorine and preferably from about 1.77 to 7.09 g active chlorine per mole of polysaccharide ASU. When sodium hypochlorite is used it is added in a limited amount of up to 40 mole percent based on the moles of polysaccharide ASU, more particularly from about 1 to 40 mole percent and preferably from about 5 to 20 mole percent based on the moles of polysaccharide ASU. By limiting the amount of oxidant and controlling its rate of addition under defined aqueous conditions, the polysaccharide C-6 aldehyde derivatives are selectively prepared at effective high levels while minimizing carboxyl formation.

**[0027]** The oxidation reaction may be carried out in an organic, or preferably, aqueous slurry or solution of the polysaccharide. This is accomplished by the slow and controlled addition of the oxidant to the aqueous slurry or solution of the polysaccharide containing a mediating quantity of the nitroxyl radical so as to keep the reaction temperature in the desired temperature range of at or below the maximum temperature of  $15^\circ\text{C}$ , particularly  $0$  to  $15^\circ\text{C}$  and more particularly  $5$  to  $10^\circ\text{C}$  and the pH is maintained at 8.0 to 10.5 and particularly 9 to 10. The oxidant can be added as the hypochlorite or hypobromite, e.g., sodium hypochlorite or sodium hypobromite, or the hypobromite can be formed in situ by first adding sodium bromide and then adding the sodium hypochlorite solution to generate the hypobromite in situ.

**[0028]** The oxidation may be carried out either in the granular state (slurry reaction) for water insoluble polysaccharides or in the solution state for soluble polysaccharides. The slurry reactions are typically performed at up to 40% solids, i.e., 0.1 to 40% solids, more particularly, 20 to 30%, while homogeneous reactions are carried out at up to 30% solids. i.e., 0.1 to 30% solids and more particularly at 5 to 15% solids.

**[0029]** The importance of carrying out the selective oxidation of polysaccharides under the defined conditions of this invention is that oxidized polysaccharides are produced with high levels of C-6 aldehyde functionality and minimal

carboxylic acid formation. These products particularly will have C-6 aldehyde groups in amounts of up to about 15 mole %, and more particularly from about 1 to 15 mole % based on the moles of polysaccharide ASU. Preferably where a slurry reaction is used, the aldehyde content will be up to about 7 mole %, more particularly from about 1 to 7 mole % based on the moles of polysaccharide ASU, whereas when dispersion oxidation is used, the aldehyde content will be up to about 15 mole % and more particularly from about 1 to 15 mole % based on the moles of polysaccharide ASU. The high or effective levels of aldehyde can be defined by aldehyde to carboxylic acid ratios of greater than or equal to 0.5 (based on the moles of polysaccharide ASU of each functionality) and preferably greater than or equal to 1.0. These aldehyde levels are particularly effective when using the derivatives as paper strength additives. Minimal carboxylic acid levels will typically be from about 0 to 20 mole % based on the moles of polysaccharide ASU.

**[0030]** Novel amphoteric C-6 aldehyde derivatives are produced when cationic polysaccharides are selectively oxidized by the process of this invention. Preferably for paper applications, the amphoteric product will have a net, cationic charge. The amount of cationic group can be varied and generally from about 0.5 to 25 mole % and preferably from about 1 to 10 mole % of cationic group based on the moles of polysaccharide ASU will be used. Preferably for paper applications, the amphoteric product will have a net cationic charge.

**[0031]** Before use in paper applications, slurry oxidized products can be batch or jet-cooked into dispersed liquids. Dispersion generated products, meanwhile, can be used as is. Slurry or dispersion oxidized products can be converted to cold water soluble form, if desired.

**[0032]** The aldehyde derivatives of this invention are useful as wet, temporary wet and dry strength additives in papermaking. The polysaccharide aldehyde derivatives may be used as beater additives, although their addition to the pulp may occur at any point in the papermaking process prior to the ultimate conversion of the wet pulp into a dry web or sheet. Thus, for example, they may be added to the pulp while the latter is in the hydropulper, beater, various stock chests or headbox. The derivative may also be sprayed or applied onto the wet web either as a dispersion or uncooked slurry. It is also envisioned that the aldehyde derivatives of this invention can be applied to the already formed paper sheet by such on machine applications as size press, calender stack or via off machine coating processes.

**[0033]** The aldehyde derivatives may effectively be used for addition to pulp prepared from any type of cellulosic fibers, synthetic fibers or combinations thereof. Among the cellulosic materials which may be used are bleached and unbleached soda, neutral sulfite, semi-chemical chemiground wood, ground wood or any combinations of these fibers. Fibers of the viscous rayon or regenerated cellulose type may also be used as well as recycled waste paper, if desired.

**[0034]** Any desired inert mineral fillers may be added to the pulp which contains the polysaccharide aldehydes of this invention. Such materials include clay, titanium dioxide, talc, calcium carbonate, calcium sulfate and diatomaceous earths. Other additives commonly introduced into paper may also be added to the pulp, for example dyes, pigments, sizing additives such as rosin or synthetic internal size, alum, anionic retention aids, microparticle systems, etc.

**[0035]** The proportion of the polysaccharide aldehyde derivative to be incorporated into the paper pulp may vary in accordance with the particular pulp involved and the properties desired. In general, it is desired to use about 0.05 to 15% and preferably about 0.1 to 5% of the derivative by weight based on the dry weight of the pulp. Within the preferred range, the precise amount which is used will depend upon type of pulp being used, the specific operating conditions, the particular end use for which the paper is intended and the particular property to be imparted.

**[0036]** The following examples will more fully illustrate the embodiments of this invention. In the examples, all parts and percentages are by weight and all temperatures in degrees Celsius unless otherwise noted.

#### EXAMPLE 1

##### Oxidation procedure on granular starch in aqueous slurry:

**[0037]** The oxidation was carried out in aqueous conditions using a 4-neck, round-bottom flask equipped with an overhead stirrer using the following procedure. The nitroxyl radical, TEMPO (0.44 g; 1 mole percent based on moles of starch ASU) and sodium bromide (2.9 g; 10 mole percent) were added to an aqueous starch slurry [50 g fluidity cationic waxy maize starch (45.5 g dry; 0.28 mole ASU) in 100 mL water] and the system was cooled to below 5°C with an ice-water bath. The pH of the mixture was adjusted to 9.5 with sodium hydroxide (4% solution). Sodium hypochlorite (24.8 g; 4.2% solution: 5 mole %), whose pH was also adjusted to 9.5, was then introduced into the reaction mixture by dropwise addition at a rate so as to maintain the temperature of the reaction mixture <15°C with an ice-water bath (ca. 10 minutes). The pH of the slurry was held constant at 9.5 through this addition process by the addition of 0.99 N sodium hydroxide solution (3.05 mL) using a Brinkmann Metrohm 718 STAT Titrimo (pH-stat). The oxidation was essentially complete once all of the hypochlorite solution was added and the pH of the system had stabilized. A small volume of ethyl alcohol (10 mL) was then introduced at this stage to ensure that all of the hypochlorite had been consumed. Finally, the pH of the mixture was lowered to the 4.5 to 5.0 range with hydrochloric acid. The oxidized starch products were recovered by filtration and extensively washed by re-suspension in a 60/40 water/ethanol (v/v) mixture. They were then recovered by filtration, washed with water and air dried in a low humidity environment.

Determination of aldehyde content:

[0038] Aldehyde content in oxidized starch was determined using hydroxylamine hydrochloride titration via oxime derivatization according to the following reaction and the procedure.



Starch slurry (87.5 g; 10 weight percent), oxidized as described above, was pH adjusted to 4 with aqueous HCl. To this stirred solution, a large excess of an aqueous solution of 0.3 M hydroxylamine hydrochloride solution (ca. 50 mL at pH 4) was added dropwise. During the reaction the pH of the mixture was maintained at 4 via titration with a 0.99 N NaOH solution using a pH stat. Following the completion of hydroxylamine hydrochloride addition, stirring was continued until no further reduction in pH of the solution could be detected.

[0039] The aldehyde content of the starch sample was calculated to be 2.3 mole % based on moles of starch ASU by the total consumption of NaOH (1.27 mL) using the following equation:

$$\text{mole \% -CHO} = \frac{(\text{mL of NaOH titrant} \times \text{N of NaOH}) / 1000 \times 100}{\text{moles of starch ASU}}$$

[0040] Alternatively aldehyde content of the oxidized starch could also be estimated from the residual oxidant that was not spent in -COOH formation as described below.

$$\text{Mole \% -CHO} = \text{total mole \% oxidant added} - (\text{mole \% -COOH}) \times 2$$

Determination of carboxylic acid content:

[0041] The carboxylic acid formed during the oxidation was calculated from the amount of NaOH titrant consumed to maintain the pH of the slurry at the reaction pH. This provides a direct measure of the carboxylic acid generated on starch which was 3.05 mL, corresponding to 1.1 mole percent based on moles of starch ASU. The following equation was used for the calculation:

$$\text{mole \% -COOH} = \frac{(\text{mL of NaOH titrant} \times \text{N of NaOH}) / 1000 \times 100}{\text{moles of starch ASU}}$$

## EXAMPLE 2

Oxidation on dispersed (cooked) starch:

[0042] To a 700 g cooked dispersion of 6 weight percent fluidity waxy maize starch (42 g starch or 0.26 moles of ASU) in water was added 55 mg of 4-acetamido-TEMPO (0.1 mole % based on moles of starch ASU) and 2.67 g sodium bromide (10 mole percent). The homogeneous solution was cooled to 5°C and its pH was raised to 9.5 using aqueous sodium hydroxide. Sodium hypochlorite (44.7 g of 13% solution; 30 mole %), whose pH was also adjusted to 9.5, was then introduced into the reaction mixture by dropwise addition at a rate so as to maintain the temperature of the reaction mixture at <15°C with an ice-water bath (ca. 20 minutes). The pH of the solution was held constant at 9.5 throughout this addition process with 0.99 N sodium hydroxide solution (20.8 mL) using a Brinkmann Metrohm 718 STAT Titrimo (pH-stat). The oxidation was essentially complete once all of the hypochlorite solution was added and the pH of the system had stabilized. A small volume of ethyl alcohol (20 mL) was then introduced at this stage to ensure that all of the Hypochlorite had been consumed. Finally, the pH of the mixture was lowered to the 4.5 to 5.0 range using hydrochloric acid. At this stage 100 g of the solution was set aside for -CHO determination. The oxidized starch was then recovered by slow precipitation into ethyl alcohol (five times the volume) with rapid stirring. The precipitate was filtered off, washed with ethanol and air dried in a low humidity environment.

[0043] The -COOH content of the starch was determined from the titration during the oxidation as described in Example 1 to be 8 mole % based on moles of starch ASU. Aldehyde content in the sample was determined as described in

Example 1 by hydroxylamine hydrochloride titration of 50 g aliquots of the solution set aside after the oxidation (5.5 weight percent starch) which consumed an average of 2.40 mL NaOH (0.99 N) corresponding to 14 mole % based on moles of starch ASU.

### 5 EXAMPLE 3

[0044] The procedure described in Example 1 was repeated several times under similar conditions on fluidity cationic waxy maize starch (3-chloro-2-hydroxypropyltrimethylammonium chloride modified, 5.3 mole % based on moles of starch ASU) in order to determine the effect of oxidation pH and temperature on the C-6 aldehyde (-CHO) and carboxyl (-COOH) functional content of the products. In these cases the addition rate of the NaOCl oxidant was adjusted so as to keep the reactions at prescribed temperatures using an external cooling bath. Table 1 lists the conditions and the results obtained.

TABLE 1 The effect of oxidation conditions on the C-6 aldehyde and carboxylic acid content of fluidity cationic waxy maize in the slurry state

15	Oxidant			Product		
	Active chlorine equivalent (g/mole)*	NaOCl (mole%)*	Oxidation temperature (°C)	Oxidation pH	-CHO content (mole%)*	-COOH content (mole%)*
20	3.55	10	5	10.5	42	2.9
	3.55	10	5	8.5	4.5	2.7
	3.55	10	5	9.5	4.8	2.6
	3.55	10	10	9.5	4.4	2.8
25	3.55	10	15	9.5	4.1	2.9
	3.55	10	25	9.5	1.4	4.3
* based on moles of starch ASU						

### 30 EXAMPLE 4

[0045] The procedure described in Example 1 was repeated several times on either fluidity waxy maize or fluidity cationic waxy maize granular starches in the slurry state to determine the effect of various targeted oxidation levels on C-6 aldehyde (-CHO) and carboxyl (-COOH) functional content of the products. The results are listed in Table 2.

TABLE 2 Oxidation of fluidity waxy maize and fluidity cationic waxy maize starches in the slurry and C-6 functional content of products

	Oxidant		Starch		Product	
	Sample #	Active chlorine equivalent (g/mole)*	NaOCl (mole %)	Cationic content (mole %)*	-CHO content (mole %)*	-COOH content (mole %)*
40	A	14.18	40	5.7	4.7	18.0
	B	10.64	30	0	5.3	12.0
45	C	7.09	20	5.7	5.9	7.1
	D	7.09	20	0	5.9	7.1
	E	3.55	10	5.7	4.1	3.0
	F	3.55	10	0	42	2.9
50	G	1.77	5	0	2.8	1.1
	H	1.77	5	3.8	2.8	1.1
* based on moles of starch ASU						

### 55 EXAMPLE 5

[0046] The procedure described in Example 2 was repeated several times under similar conditions on either fluidity waxy maize or fluidity cationic waxy maize starches in the dispersed state to determine the effect of various targeted



oxidation levels on C-6 aldehyde (-CHO) and carboxyl (-COOH) functional content of the products. The results are listed in Table 3.

TABLE 3 Oxidation on fluidity waxy maize and fluidity cationic waxy maize starches in the dispersed state and the C-6 functional contents of products.

	Oxidant		Starch	Product	
Sample #	Active chlorine equivalent (g/ mole)*	NaOCl (mole %) *	Cationic content (mole %)*	-CHO content (mole %)*	-COOH content (mole %)*
I	14.18	40	5.7	12.0	14.0
J	10.64	30	3.8	12.0	8.8
K	7.09	20	0	11.0	4.7
L	7.09	20	3.8	10.0	4.8
M	5.32	15	5.7	8.7	3.1
N	3.55	10	5.7	6.9	1.6
O	3.55	10	3.8	6.9	1.5
P	1.77	5	3.8	4.0	0.5

\* based on moles of starch ASU

#### EXAMPLE 6

[0047] Wet and dry tensile strength performance imparted by several of the cationic starch aldehyde derivatives prepared as in Examples 4 and 5 were evaluated on 18 lb/3300 sq.ft handsheets made from 100% Northern Softwood Kraft pulp (650CSF) on a Noble and Wood Sheet Mold at pH 6-7. The addition level of the starch was 5 and 10 lb/ton. Dispersion oxidized products were added to the cellulose pulp directly after the reaction, while slurry products were cooked at 100°C for 20 to 30 minutes at 1 weight percent and at pH 4.5 prior to addition. One inch wide strips were cut from handsheets and tested for Initial wet tensile strength and dry tensile strength at the breaking point according to the TAPPI Standard Test Method T 456. The results are given in Table 4.

TABLE 4 Wet and dry tensile strength of handsheets treated with cationic starch aldehyde derivatives prepared in Examples 4 and 5.

Sample #	Wet tensile strength at 5lb/T (g/in)	Dry tensile strength at 5lb/T (g/in)	Wet tensile strength at 10lb/T (g/in)	Dry tensile strength at 10lb/T (g/in)
Unoxidized cationic waxy maize				
E	20	1400	30	1600
H	153	1985	252	2048
M	110	1967	155	1884
N	304	1863	368	2398
P	254	1971	332	2142
O	183	2005	257	2206
	209	1875	313	2249

#### EXAMPLE 7

##### Preparation of pullulan aldehyde derivatives:

[0048] The oxidation was carried out in homogeneous aqueous conditions similar to described in Example 2 as follows. The nitroxyl radical, 4-acetamido TEMPO (19 mg) and sodium bromide (1.1g) were added to 750 g solution of 4.5 wt% pullulan (from Polysciences Inc.). The system was cooled to < 10°C with an ice-water bath and its pH was adjusted to 9 with aqueous sodium hydroxide. 16.2 g sodium hypochlorite (as 10.6% aqueous solution), whose pH was also adjusted to 9, was then introduced into the vigorously stirred reaction mixture dropwise at a rate so as to maintain the temperature of the reaction mixture <10°C. The pH of the solution was held constant at 9 throughout this addition process by titration with 0.49 N sodium hydroxide solution (10.7 mL) using a Brinkmann Metrohm 718 STAT Titrino (pH-stat). The oxidation

was essentially complete once all of the hypochlorite solution was added and the pH of the system had stabilized (ca. 15 min). A small amount of ethyl alcohol (5 mL) was introduced at this stage to ensure that all of the hypochlorite had been consumed. Finally, the pH of the mixture was lowered to between 4.0 to 4.5 with hydrochloric acid. At this stage about 100 g of the solution was set aside for aldehyde content determination. The oxidized pullulan was then recovered by slow precipitation into ethyl alcohol. The precipitate was filtered off, washed with ethanol and air dried in a low humidity environment

[0049] Aldehyde content in the sample was determined as described in Example 1 by hydroxylamine hydrochloride titration of 30 g aliquots of the solution set aside after the oxidation (1.3 g oxidized pullulan) which consumed an average of 3.8 mL NaOH (0.1 N) corresponding to 4.8 mole % based on moles of pullulan ASU. The -COOH content of the pullulan was determined from the titration during the oxidation as described in Example 1 to be 2.5 mole % based on moles of pullulan ASU.

#### EXAMPLE 8

##### Preparation of aldehyde derivatized guar gum:

[0050] Using a procedure similar to described in Example 7, native guar gum (Procol U from Polypro Chemical Inc.) was oxidized in aqueous solution in the following manner. 6.4 g NaOCl (as 6.5% solution) was added slowly to a cooled and stirred solution of 0.5 g guar gum, 39 mg 4-acetamido TEMPO and 0.19 g sodium bromide in 800 mL water at pH 9.5. The solution pH was maintained at 9.5 throughout the reaction by the addition of 0.99 M NaOH solution using a Brinkman Metrohm 718 pH-stat Titrino until no further consumption took place (about 45 minutes). The reaction was then quenched with ethyl alcohol (5 mL) and worked up as described in Example 7.

[0051] Aldehyde and carboxyl content of the modified guar gum was determined by similar procedures to those described in Example 7 and was found to be 5.6 mol% and 5.6 mol% per guar ASU, respectively.

#### EXAMPLE 9

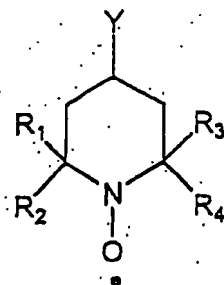
[0052] 2-Hydroxyethyl cellulose ( $M_v$  - 90,000 and DS 1.5 from Aldrich Chemical Co.) was also oxidized in aqueous solution under similar conditions to those described in Example 7 as follows. 26.8 g NaOCl (as 13 % solution) was added slowly to a cooled and stirred solution of 28.8 g 2-hydroxyethyl cellulose, 34 mg 4-acetamido TEMPO and 1.6 g sodium bromide in 800 mL water at pH 9.5. The solution pH was maintained at 9.5 throughout the reaction by the addition of 0.99 M NaOH solution using a pH-stat until no further consumption took place. The reaction was then terminated with ethyl alcohol (5 mL) and worked up as described in Example 7.

[0053] Aldehyde and carboxyl content of the oxidized 2-hydroxyethyl cellulose was determined by similar procedures to those described in Example 7 and was found to be 3 mol% and 17 mol% per ASU respectively.

#### Claims

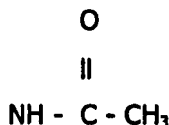
1. A method for preparing polysaccharide aldehyde derivatives having maximum effective aldehyde content comprising oxidizing polysaccharide in an aqueous solution with an oxidant having an equivalent oxidizing power of up to 14.18 g of active chlorine per mole of polysaccharide ASU and from 0.001 to 20 mole %, based on the moles of polysaccharide ASU, of nitroxyl radical, the reaction being carried out by slow and controlled addition of the oxidant to the aqueous slurry or solution of the polysaccharide containing the nitroxyl radical so as to keep the temperature at or less than 15°C and the pH of from 8.0 to 10.5, the resulting product having up to 15 mole % of C-6 aldehyde groups per mole of polysaccharide ASU and minimal carboxylic acid content.

2. The method of claim 1 wherein the nitroxyl radical has the formula:



where Y is H, OH or NH-C(O)-CH<sub>3</sub> and each of the R groups represent the same or different alkyl groups of 1 to 18 carbon atoms and more particularly methyl groups.

3. The method of claims 1 - 2 wherein the oxidant has an equivalent oxidizing power of from 0.35 to 14.18 g of active chlorine per mole of polysaccharide ASU.
4. The method of claims 1 - 3 wherein the oxidant is sodium hypochlorite or sodium hypobromite.
5. The method of claims 1 - 4 wherein the resulting product has from 1 to 15 mole % of aldehyde groups per mole of polysaccharide ASU and from 0 to 20 mole % of carboxylic acid content per mole of polysaccharide ASU.
6. The method of claims 1 - 5, wherein in the nitroxyl radical X is H or



7. The method of claims 1-6 wherein the oxidation is carried out in a slurry reaction.
8. The method of claim 1 - 7 wherein the resulting product has from 1 to 7 mole % of aldehyde groups per mole of polysaccharide ASU.
9. The method of claim 1 - 8 wherein the oxidation is carried out in the dispersed state.
10. The method of claims 1-9 wherein from 5 to 20 mole % of oxidant is used, the reaction temperature is from 5 to 10°C and the pH is from 9 to 10.
11. The method of claim 1-10 wherein the resulting product has from 1 to 15 mole % of aldehyde groups per mole of polysaccharide ASU.
12. The method of claim 11 wherein the polysaccharide is modified with a cationic group.
13. The method of claims 1 - 12 wherein the oxidant is hypobromite formed in situ by the addition of sodium bromide and sodium hypochlorite.
14. The polysaccharide aldehyde derivative produced by the method of claims 1 - 13.
15. An amphoteric polysaccharide aldehyde which has from 0.5 to 25 mole % of cationic groups based on the moles of polysaccharide ASU, from 1 to 15 mole % of C-6 aldehyde content based on the moles of polysaccharide ASU and from 0.5 to 20 mole % of carboxylic acid content based on the moles of polysaccharide ASU.
16. The amphoteric polysaccharide aldehyde of claim 15 wherein the cationic and carboxyl content is present in amounts that provide a net cationic charge.

17. In a method of making paper having wet strength, temporary wet strength, and dry strength the step which comprises adding as a strength aid to the paper an effective amount of the polysaccharide aldehyde derivative prepared by the method of claim 1 - 13.

5 18. Paper produced by the method of claim 17.

19. A method of producing a polysaccharide aldehyde derivative by claims 1-13 wherein the polysaccharide aldehyde derivative is a starch aldehyde derivative and the polysaccharide is starch.

10 20. The amphoteric polysaccharide aldehyde derivative of Claims 15-16 wherein the amphoteric polysaccharide aldehyde derivative is a starch aldehyde derivative.

21. The method of making paper of Claim 17 wherein the polysaccharide aldehyde derivative is a starch aldehyde derivative.

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22. The paper produced by the method of Claim 17 wherein the polysaccharide aldehyde derivative is a starch aldehyde derivative.

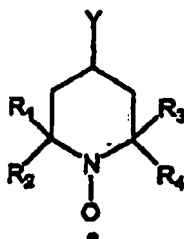
## 20 Revendications

1. Procédé pour la préparation de dérivés aldéhydiques de polysaccharides ayant une teneur en aldéhyde efficace maximale, comprenant l'oxydation d'un polysaccharide en solution aqueuse avec un oxydant ayant un pouvoir oxydant équivalent d'au plus 14,18 g de chlore actif par mole d'UAS de polysaccharide et 0,001 à 20 % en moles, par rapport aux moles d'UAS de polysaccharide, de radical nitroxyle, la réaction étant conduite par addition lente et réglée de l'oxydant à la suspension ou solution aqueuse du polysaccharide contenant le radical nitroxyle de manière à maintenir la température à une valeur inférieure ou égale à 15°C et le pH entre 8,0 et 10,5, le produit résultant ayant jusqu'à 15 % en moles de groupes aldéhyde C-6 par mole d'UAS de polysaccharide et une teneur minimale en acide carboxylique.

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2. Procédé selon la revendication 1, dans lequel le radical nitroxyle répond à la formule :

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45 où Y est H, OH ou NH-C(O)-CH<sub>3</sub>, et chacun des groupes R représente des groupes alkyle identiques ou différents de 1 à 18 atomes de carbone et plus particulièrement des groupes méthyle.

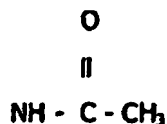
3. Procédé selon les revendications 1 et 2, dans lequel l'oxydant a un pouvoir oxydant équivalent de 0,35 à 14,18 g de chlore actif par mole d'UAS de polysaccharide.

50 4. Procédé selon les revendications 1 à 3, dans lequel l'oxydant est l'hypochlorite de sodium ou l'hypobromite de sodium.

5. Procédé selon les revendications 1 à 4, dans lequel le produit résultant contient 1 à 15 % en moles de groupes aldéhyde par mole d'UAS de polysaccharide et 0 à 20 % en moles d'acide carboxylique par mole d'UAS de polysaccharide.

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6. Procédé selon les revendications 1 à 5, dans lequel, dans le radical nitroxyle, X est H ou



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7. Procédé selon les revendications 1 à 6, dans lequel l'oxydation est effectuée dans une réaction en suspension.
- 10 8. Procédé selon les revendications 1 à 7, dans lequel le produit résultant contient 1 à 7 % en moles de groupes aldéhyde par mole d'UAS de polysaccharide.
9. Procédé selon les revendications 1 à 8, dans lequel l'oxydation est conduite à l'état dispersé.
- 15 10. Procédé selon les revendications 1 à 9, dans lequel on utilise 5 à 20 % en moles d'oxydant, la température de réaction est de 5 à 10°C et le pH est de 9 à 10.
11. Procédé selon les revendications 1 à 10, dans lequel le produit résultant contient 1 à 15 % en moles de groupes aldéhyde par mole d'UAS de polysaccharide.
- 20 12. Procédé selon la revendication 11, dans lequel le polysaccharide est modifié avec un groupe cationique.
13. Procédé selon les revendications 1 à 12, dans lequel l'oxydant est un hypobromite formé in situ par addition de bromure de sodium et d'hypochlorite de sodium.
- 25 14. Dérivé aldéhydique de polysaccharide, produit par le procédé des revendications 1 à 13.
15. Aldéhyde de polysaccharide amphotère qui contient 0,5 à 25 % en moles de groupes cationiques par rapport aux moles d'UAS de polysaccharide, 1 à 15 % en moles d'aldéhyde C-6 par rapport aux moles d'UAS de polysaccharide et 0,5 à 20 % en moles d'acide carboxylique par rapport aux moles d'UAS de polysaccharide.
- 30 16. Aldéhyde de polysaccharide amphotère selon la revendication 15, dans lequel les composants cationique et carboxyle sont présents en des quantités qui donnent une charge nette cationique.
- 35 17. Dans un procédé de fabrication de papier doué de résistance à l'humidité, de résistance à l'humidité temporaire et de résistance à sec, l'étape qui consiste à ajouter au papier, comme adjuvant de renforcement, une quantité efficace du dérivé aldéhydique de polysaccharide préparé par le procédé des revendications 1 à 13.
- 40 18. Papier produit par le procédé de la revendication 17.
19. Procédé de production d'un dérivé aldéhydique de polysaccharide selon les revendications 1 à 13, dans lequel le dérivé aldéhydique de polysaccharide est un dérivé aldéhydique d'amidon et le polysaccharide est l'amidon.
- 45 20. Dérivé aldéhydique de polysaccharide amphotère selon les revendications 15 et 16, dans lequel le dérivé aldéhydique de polysaccharide amphotère est un dérivé aldéhydique d'amidon.
21. Procédé de fabrication de papier selon la revendication 17, dans lequel le dérivé aldéhydique de polysaccharide est un dérivé aldéhydique d'amidon.
- 50 22. Papier produit par le procédé selon la revendication 17, dans lequel le dérivé aldéhydique de polysaccharide est un dérivé aldéhydique d'amidon.

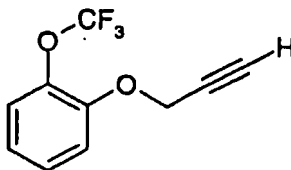
#### Patentansprüche

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1. Verfahren zur Herstellung von Polysaccharidaldehydderivaten mit maximalem effektivem Aldehydgehalt, umfassend Oxidieren von Polysaccharid in einer wässrigen Lösung mit einem Oxidationsmittel, das eine Oxidationskraft hat, die bis zu 14,18 g aktivem Chlor pro mol Polysaccharid ASU äquivalent ist, und 0,001 bis 20 mol-%, bezogen auf

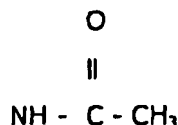
die Mol an Polysaccharid ASU, Nitroxylradikal, wobei die Reaktion durch langsame und kontrollierte Zugabe des Oxidationsmittels zu der wässrigen Aufschlämmung oder Lösung des Polysaccharids, die das Nitroxylradikal enthält, durchgeführt wird, so dass die Temperatur bei 15°C oder weniger und der pH von 8,0 bis 10,5 gehalten wird, wobei das resultierende Produkt bis zu 15 mol-% C-6-Aldehydgruppen pro mol Polysaccharid ASU und einen minimalen Carbonsäuregehalt hat.

2. Verfahren nach Anspruch 1, wobei das Nitroxylradikal die folgende Formel hat:



worin Y H, OH oder NH-C(O)-CH<sub>3</sub> ist und die R-Gruppen jeweils die gleichen oder unterschiedliche Alkylgruppen mit 1 bis 18 Kohlenstoffatomen und insbesondere Methylgruppen darstellen.

3. Verfahren nach Anspruch 1 bis 2, wobei das Oxidationsmittel eine Oxidationskraft, die 0,35 bis 14,18 g aktivem Chlor pro mol Polysaccharid ASU äquivalent ist.
4. Verfahren nach den Ansprüchen 1 bis 3, wobei das Oxidationsmittel Natriumhypochlorit oder Natriumhypobromit ist.
5. Verfahren nach den Ansprüchen 1 bis 4, wobei das resultierende Produkt 1 bis 15 mol-% Aldehydgruppen pro mol Polysaccharid ASU hat und 0 bis 20 mol-% Carbonsäuregehalt pro mol Polysaccharid ASU hat.
6. Verfahren nach den Ansprüchen 1 bis 5, wobei im Nitroxylradikal X H oder



ist.

7. Verfahren nach den Ansprüchen 1 bis 6, wobei die Oxidation in einer Aufschlämmungsreaktion durchgeführt wird.
8. Verfahren nach Anspruch 1 bis 7, wobei das resultierende Produkt 1 bis 7 mol-% Aldehydgruppen pro mol Polysaccharid ASU hat.
9. Verfahren nach Anspruch 1 bis 8, wobei die Oxidation im dispergierten Zustand durchgeführt wird.
10. Verfahren nach den Ansprüchen 1 bis 9, wobei 5 bis 20 mol-% Oxidationsmittel verwendet werden, die Reaktionstemperatur 5 bis 10°C ist und der pH 9 bis 10 ist.
11. Verfahren nach Anspruch 1 bis 10, wobei das resultierende Produkt 1 bis 15 mol-% Aldehydgruppen pro mol Polysaccharid ASU hat.
12. Verfahren nach Anspruch 11, wobei das Polysaccharid mit einer kationischen Gruppe modifiziert ist.
13. Verfahren nach den Ansprüchen 1 bis 12, wobei das Oxidationsmittel Hypobromit ist, das in situ durch Zugabe von Natriumbromid und Natriumhypochlorit gebildet wird.

14. Polysaccharidaldehydderivat, das durch das Verfahren nach den Ansprüchen 1 bis 13 produziert wird.
15. Amphoterer Polysaccharidaldehyd, der 0,5 bis 25 mol-% kationische Gruppen, bezogen auf die Mol an Polysaccharid ASU, 1 bis 15 mol-% C-6-Aldehydgehalt, bezogen auf die Mol an Polysaccharid ASU, und 0,5 bis 20 mol-% Carbonsäuregehalt, bezogen auf die Mol an Polysaccharid ASU, hat.
16. Amphoterer Polysaccharidaldehyd nach Anspruch 15, wobei der Kationen- und Carboxylgehalt in Mengen vorliegt, dass eine kationische Nettoladung bereitgestellt wird.
17. In einem Verfahren zur Herstellung von Papier, das Nassfestigkeit, temporäre Nassfestigkeit und Trockenfestigkeit hat, den Schritt, der Zugabe als Festigkeitshilfsmittel zu dem Papier einer wirksamen Menge des Polysaccharidaldehydderivats, das nach dem Verfahren von Anspruch 1 bis 13 hergestellt ist, umfasst.
18. Papier, das durch das Verfahren nach Anspruch 17 produziert wird.
19. Verfahren zur Herstellung eines Polysaccharidaldehydderivats nach den Ansprüchen 1 bis 13, wobei das Polysaccharidaldehydderivat ein Stärkealdehydderivat ist und das Polysaccharid Stärke ist.
20. Amphoterer Polysaccharidaldehydderivat nach Anspruch 15 bis 16, wobei das amphotere Polysaccharidaldehydderivat ein Stärkealdehydderivat ist.
21. Verfahren zur Herstellung von Papier nach Anspruch 17, wobei das Polysaccharidaldehydderivat ein Stärkealdehydderivat ist.
22. Papier, das durch das Verfahren nach Anspruch 17 produziert wurde, wobei das Polysaccharidaldehydderivat ein Stärkealdehydderivat ist.